



Copy of Amended Claims indicating the Amendments

21. (Twice Amended) A (co)polymer, comprising:

one or more free radically (co)polymerizable monomers, wherein the polymer exhibits a stereochemistry and microstructure, as defined by tacticity and sequence distribution, of a material formed by a free radical polymerization process, and displays a molecular weight distribution of less than 2.0; and

a residue of an initiator, wherein the residue is not a residue of a carbon tetrachloride initiator;

a thermally stable end group selected from the group consisting of a halogen, Cl, Br, I, OH, CN, N₃, OR¹⁰, SR¹⁴, SeR¹⁴, OC(=O)R¹⁴, OP(=O)R¹⁴, OP(=O)(OR¹⁴)₂, O-N(R¹⁴)₂, carboxylic acid halide, H, NH₂, COOH, and olefinic end groups, where R¹⁴ is aryl or a straight or branched C₁-C₂₀ alkyl group or where an N(R¹⁴)₂ group is present, the two R¹⁴ groups may be joined to form a 5-, 6- or 7- member heterocyclic ring, and R¹⁰ is an alkyl of from 1 to 20 carbon atoms or an alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be replaced by a halide, alkenyl of from 2 to 20 carbon atoms, alkynyl of from 2 to 10 carbon atoms, phenyl, phenyl substituted with from 1 to 5 halogen atoms or alkyl groups with from 1 to 4 carbon atoms, aralkyl, aryl, aryl substituted alkyl, in which the aryl group is phenyl or substituted phenyl and the alkyl group is from 1 to 6 carbon atoms; possesses thermally stable residues of a polymerization initiator at each polymer end which will not thermally dissociate from the (co)polymer at temperatures below 150°C in the absence of a catalyst at predominantly each polymer chain end and

a molecular weight in excess of two monomer units.

22. (Twice Amended) The polymer of claim 21, wherein at least one of the residue and end group thermally stable residues are comprise a functional groups.

23. (Twice Amended) The polymer of claim 21, wherein the thermally stable residues and end groups can be modified to be used in subsequent chemical reactions.

24. (Amended) A block copolymer comprising two or more blocks of units obtained from free radically (co)polymerizable monomers, wherein the block copolymer has a residue from an initiator at one chain end and, at the other end of the polymer chain, a member selected from the group consisting of radically transferable atoms, radically transferable groups, halogen, Cl, Br, I, OH, CN, N₃, OR¹⁰, SR¹⁴, SeR¹⁴, OC(=O)R¹⁴, OP(=O)R¹⁴, OP(=O)(OR¹⁴)₂, O-N(R¹⁴)₂, carboxylic acid halide, H, NH₂, COOH, and olefinic end groups, where R¹⁴ is aryl or a straight or branched C₁-C₂₀ alkyl group or where an N(R¹⁴)₂ group is present, the two R¹⁴ groups may be joined to form a 5-, 6- or 7- member heterocyclic ring, and R¹⁰ is an alkyl of from 1 to 20 carbon atoms or an alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be replaced by a halide, alkenyl of from 2 to 20 carbon atoms, alkynyl of from 2 to 10 carbon atoms, phenyl, phenyl substituted with from 1 to 5 halogen atoms or alkyl groups with from 1 to 4 carbon atoms, aralkyl, aryl, aryl substituted alkyl, in which the aryl group is phenyl or substituted phenyl and the alkyl group is from 1 to 6 carbon atoms groups formed by conventional chemistry on said radically transferable atoms and groups formed by conventional chemistry on said radically transferable groups.

26. (Twice Amended) A block copolymer, comprising:

at least two units obtained from one or more radically (co)polymerizable monomers, wherein each unit is substantially similar in microstructure and length such that the molecular weight distribution is less than 2; and

a residue from an initiator in the copolymer connecting the units; and;

~~at each chain end, a member selected from the group consisting of radically transferable atoms, radically transferable groups, halogen, Cl, Br, I, OH, CN, N₃, OR¹⁰, SR¹⁴, SeR¹⁴, OC(=O)R¹⁴, OP(=O)R¹⁴, OP(=O)(OR¹⁴)₂, O-N(R¹⁴)₂, carboxylic acid halide, H, NH₂, COOH, and olefinic end groups, where R¹⁴ is aryl or a straight or branched C₁-C₂₀ alkyl group or where an N(R¹⁴)₂ group is present, the two R¹⁴ groups may be joined to form a 5-, 6- or 7- member heterocyclic ring, and R¹⁰ is an alkyl of from 1 to 20 carbon atoms or an alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be replaced by a halide, alkenyl of from 2 to 20 carbon atoms, alkynyl of from 2 to 10 carbon atoms, phenyl, phenyl substituted with from 1 to 5 halogen atoms or alkyl groups with from 1 to 4 carbon atoms, aralkyl, aryl, aryl substituted alkyl, in which the aryl group is phenyl or substituted phenyl and the alkyl group is from 1 to 6 carbon atoms groups obtained by conventional chemistry from said radically transferable atoms and groups obtained by conventional chemistry from said radically transferable groups, attached to the units.~~

27. (Twice Amended) A copolymer comprising:

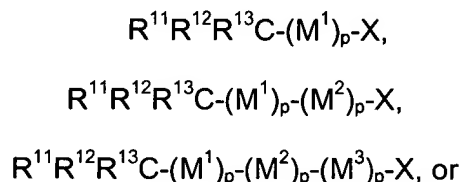
units obtained from free radically (co)polymerizable monomers, wherein the copolymer is formed by coupling two polymer chains, such that substantially each polymer chain has a residue of an initiator present on substantially each polymer chain end, wherein the polymer has a molecular weight distribution of less than 2.

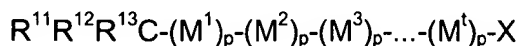
32. (Twice Amended) The block copolymer as claimed in claim 24, wherein said block copolymer is a poly(styrene-block-methyl acrylate) or a poly(methyl acrylate-block-styrene) (co)polymer ~~having a residue of an initiator molecule at an initiation site at one polymer chain end, and a radically transferable atom or group at the other polymer chain end.~~

34. (Twice Amended) The (co)polymer as claimed in claim 21, wherein said (co)polymer is selected from the group consisting of linear, monofunctional, star and telechelic polystyrenes, linear and star poly(methyl acrylate)s, poly(butyl acrylate)s, poly(methyl methacrylate)s, and polyisoprenes, wherein the (co)polymer ~~has either a residue of an initiator or a group obtained by conventional chemistry from the residue of the initiator at an initiation site, and a radically transferable atom or group at a polymer chain end, and wherein the~~ (co)polymer displays a tacticity of a polymer prepared by free radical polymerization ~~and has a molecular weight distribution of less than 2.0.~~

35. (Twice Amended) The (co)polymer claimed in claim 28, prepared by (co)polymerizing styrene and a monomer selected from methyl acrylate and methyl methacrylate to yield polymers in which the (co)polymer has a composition that ~~changes in a predictable manner~~ varies along the length of the (co)polymer based on the relative reactivity ratios of the monomers and ~~a ratio of the~~ instantaneous concentrations of the monomers during the polymerization.

38. (Twice Amended) The (co)polymer of Claim 64, having a formula:





wherein X is selected from the group consisting of Cl, Br, I, OR¹⁰, SR¹⁴, SeR¹⁴, O-N(R¹⁴)₂, S-C(=S)N(R¹⁴)₂, H, OH, N₃, NH₂, COOH, and CONH₂, halogen, OC(=O)R¹⁴, OP(=O)R¹⁴, OP(=O)(OR¹⁴)₂, O-N(R¹⁴)₂, carboxylic acid halide, and olefinic end groups, where R¹⁴ is aryl or a straight or branched C₁-C₂₀ alkyl group or where an N(R¹⁴)₂ group is present, the two R¹⁴ groups may be joined to form a 5-, 6- or 7- member heterocyclic ring, and R¹⁰ is an alkyl of from 1 to 20 carbon atoms or an alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be replaced by a halide, alkenyl of from 2 to 20 carbon atoms, alkynyl of from 2 to 10 carbon atoms, phenyl, phenyl substituted with from 1 to 5 halogen atoms or alkyl groups with from 1 to 4 carbon atoms, aralkyl, aryl, aryl substituted alkyl, in which the aryl group is phenyl or substituted phenyl and the alkyl group is from 1 to 6 carbon atoms or a group derived therefrom; and where

R¹⁰ is an alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R¹⁴ is aryl or a straight or branched C₁-C₂₀ alkyl group, and where an N(R¹⁴)₂ group is present, the two R¹⁴ groups may be joined to form a 5- or 6-membered heterocyclic ring,

R¹¹, R¹² and R¹³ are each independently selected from the group consisting of H, halogen, C₁-C₂₀ alkyl, C₃-C₈ cycloalkyl, C(=Y)R⁵, C(=Y)NR⁶R⁷, COCl, OH, CN, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C₁-C₆ alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and C₁-C₆ alkyl substituted with from 1 to 3 substituents selected from the group consisting of C₁-C₄ alkoxy, aryl, heterocyclyl, C(=Y)R⁵, C(=Y)NR⁶R⁷, oxiranyl and glycidyl,

where Y is NR⁸, S or O,

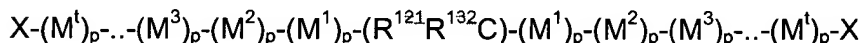
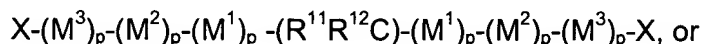
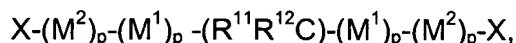
where R⁵ is an aryl or an alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; and R⁶ and R⁷ are independently H or alkyl of from 1 to 20 carbon atoms, or R⁶ and R⁷ may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring, such that no more than two of R¹¹, R¹², R¹³ are H,

R⁸ is H, a straight or branched C₁-C₂₀ alkyl or aryl, and

M¹, M², M³,... up to M^t are each a radically (co)polymerizable monomer selected such that the monomers in adjacent blocks are not identical, and p is an average degree of polymerization for each monomer and is independently selected such that the number average molecular weight of each block is from 1000 to 250,000 g/mol, and

t is an integer greater than 3.

39. (Three Times Amended) The (co)polymer of Claim 64, having a formula:

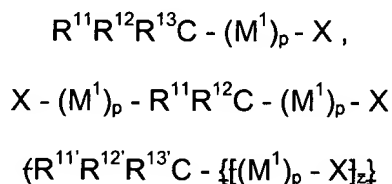


wherein R¹¹, R¹², X, M¹, M², M³,... up to M^t, t, and p are as defined above, with the proviso that the polymer chain enclosed in square brackets substituted for an original X group on the original R⁴¹.

43. (Amended) A graft or comb shaped copolymer comprising in which either or both the backbone polymer or and graft polymer segments copolymer are wherein at least one of the backbone and graft polymer segments comprise copolymers prepared from free radically (co)polymerizable monomers with, wherein the polymer segments

comprising radically polymerizable monomers comprises an predetermined average molecular weight dependent on the number of segments and the molecular weight and moles of the monomers in the segments and controlled a molecular weight distribution of the segments of less than 2.

45. (Twice Amended) A polymer of the formula:



wherein $\{(M^1)_p - X\}$ is a polymer chain where M^1 is a radically polymerizable monomer and each p is an average degree of polymerization for each block and is independently selected such that the number average molecular weight of the polymer is up to 1,000,000 g/mol,

X is selected from the group consisting of Cl, Br, I, OR^{10} , SR^{14} , $O-N(R^{14})_2$, $S-C(=S)N(R^{14})_2$, H, OH, N_3 , NH_2 , COOH and $CONH_2$, where

R^{10} is an aryl or an alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R^{14} is aryl or a straight or branched C_1 - C_{20} , alkyl group, and where an $N(R^{14})_2$ group is present, the two R^{14} groups may be joined to form a 5- or 6-membered heterocyclic ring,

R^{11} , R^{12} and R^{13} are each independently selected from the group consisting of H, halogen, C_1 - C_{20} alkyl, C_3 - C_8 cycloalkyl, $C(=Y)R^5$, $C(=Y)R^5$, $C(=Y)NR^6R^7$, COC1, OH, CN, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C_1 - C_6 alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and C_1 - C_6 alkyl substituted with from 1 to 3 substituents selected from the group consisting of C_1 - C_4 alkoxy, aryl, heterocyclyl, $C(=Y)R^5$, $C(=Y)NR^6R^7$, oxiranyl and glycidyl, where Y is NR^8 , S or O;

R⁸ is H, straight or branched C1-C20 alkyl or aryl;

R^{11'}, R^{12'} and R^{13'} are the same as R¹¹, R¹² and R¹³ with the proviso that R^{11'}, R^{12'} and R^{13'}

together comprise an additional 2 to 5 of the polymer chains;

~~Where each p is an integer independently selected such that the number average molecular weight of the polymer is up to 1,000,000 g/mol;~~

R⁵ is aryl, alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocycloxy; and R⁶ and R⁷ are independently H or alkyl of from 1 to 20 carbon atoms, or R⁶ and R⁷ may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring,

such that no more than two of R¹¹, R¹² and R¹³ are H,

~~z is from 3 to 6 and,~~

the polymer exhibits a stereochemistry characteristic of a free radical polymerized material in conjunction with a molecular weight distribution of less than 2.0.

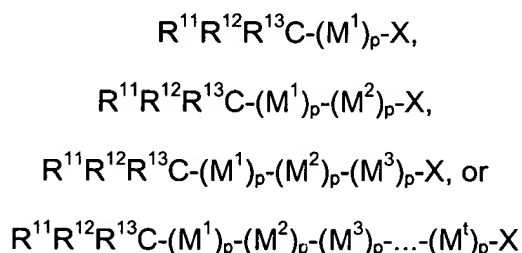
57. (Twice Amended) The (co)polymer of Claim 56, wherein the monomer which contributes oleophobic properties to the (co)polymer is selected from the group consisting of (meth)acrylate and (meth)acrylonitrile monomers.

59. (Twice Amended) The (co)polymer of Claim 58, wherein the monomer ~~unit~~ which contributes oleophobic properties to the (co)polymer is selected from the group consisting of (meth)acrylate and (meth)acrylonitrile monomers.

62. (Amended) The (co)polymer of claim 21, wherein the (co)polymer displays a molecular weight distribution of less than 1.5.

63. (Amended) The copolymer of claim 28, wherein the ~~copolymer~~ displays a molecular weight distribution of less than 1.5.

64. (Amended) A (co)polymer, exhibiting a stereochemistry and microstructure, as defined by tacticity and sequence distribution, of a polymer formed by a free radical polymerization process and displaying a molecular weight distribution of less than 2.0 and calculable number average molecular weight, having the formula:



wherein X is selected from the group consisting of Cl, Br, I, OR¹⁰, SR¹⁴, SeR¹⁴, O-N(R¹⁴)₂, S-C(=S)N(R¹⁴)₂, H, OH, N₃, NH₂, COOH, and CONH₂, ~~halogen, OC(=O)R¹⁴, OP(=O)R¹⁴, OP(=O)(OR¹⁴)₂, carboxylic acid halide, and olefinic end groups, where R¹⁴ is aryl or a straight or branched C₁-C₂₀ alkyl group or where an N(R¹⁴)₂ group is present, the two R¹⁴ groups may be joined to form a 5-, 6- or 7- member heterocyclic ring, and R¹⁰ is an alkyl of from 1 to 20 carbon atoms or an alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be replaced by a halide, alkenyl of from 2 to 20 carbon atoms, alkynyl of from 2 to 10 carbon atoms, phenyl, phenyl substituted with from 1 to 5 halogen atoms or alkyl groups with from 1 to 4 carbon atoms, aralkyl, aryl, aryl substituted alkyl, in which the aryl group is phenyl or substituted phenyl and the alkyl group is from 1 to 6 carbon atoms and groups that can be formed therefrom by conventional chemical processes, where~~

R¹⁰ is an alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R¹⁴ is aryl or a straight or

branched C₁-C₂₀ alkyl group, and where an N(R¹⁴)₂ group is present, the two R¹⁴ groups may be joined to form a 5- or 6-membered heterocyclic ring,

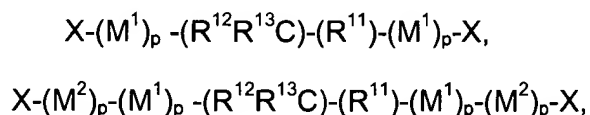
R¹¹, R¹² and R¹³ are each independently selected from the group consisting of H, halogen, C₁-C₂₀ alkyl, C₃-C₈ cycloalkyl, C(=Y)R⁵, C(=Y)NR⁶R⁷, COCl, OH, CN, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C₁-C₆ alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and C₁-C₆ alkyl substituted with from 1 to 3 substituents selected from the group consisting of C₁-C₄ alkoxy, aryl, heterocyclyl, C(=Y)R⁵, C(=Y)NR⁶R⁷, oxiranyl and glycidyl,

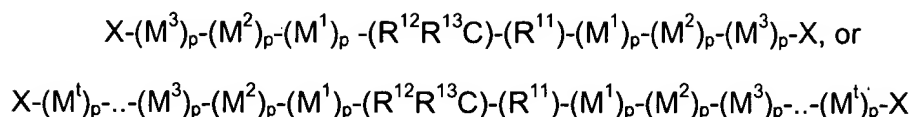
where Y is NR⁸, S or O;

where R⁵ is an aryl or an alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocycloxy; and R⁶ and R⁷ are independently H or alkyl of from 1 to 20 carbon atoms, or R⁶ and R⁷ may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring, such that no more than two of R¹¹, R¹² and R¹³ are H, and R⁸ is H, a straight or branched C₁-C₂₀ alkyl or aryl, and

M¹, M², M³,... up to M^t are each monomer units derived from radically (co)polymerizable monomer selected such that the monomers units in adjacent blocks are not identical, and t is an integer greater than 3; ~~p-for p~~ p is an average degree of polymerization for each block is independently selected such that the number average molecular weight of each block is up to 250,000 g/mol;

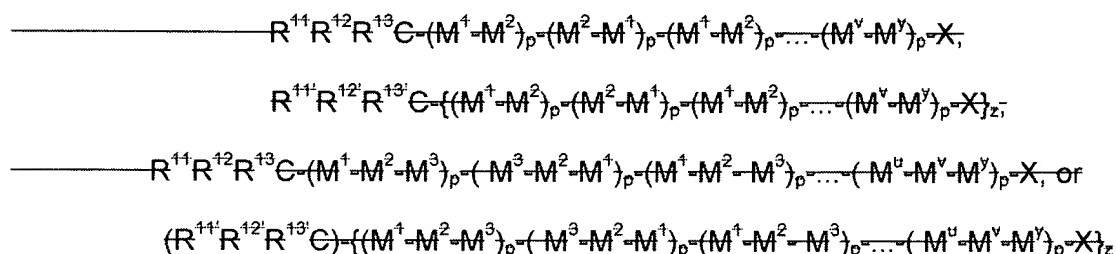
the following formulas:





wherein R^{11} , R^{12} , R^{13} , X , M^1 , M^2 , M^3 , ... up to M^t , t , and p are as defined above, with the proviso that R^{11} has a polymer chain as indicated attached thereto;

of the formulas:



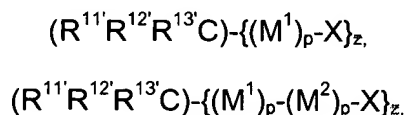
wherein z is from 2 to 6, R^{11} , R^{12} , R^{13} and X are as defined above, and where $R^{11'}$, $R^{12'}$ and $R^{13'}$ are the same as R^{11} , R^{12} and R^{13} with the proviso that $R^{11'}$, $R^{12'}$ and $R^{13'}$ combined have from 1 to 5 of the polymer chains enclosed in brackets attached thereto and the C has only one of the polymer chains enclosed in brackets attached thereto,

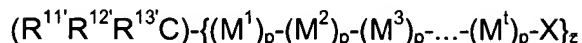
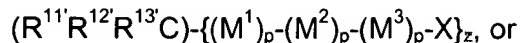
M^1 , M^2 and M^3 are monomer units derived from different radically-(co)polymerizable monomers, and M^u is one of M^1 or M^2 or M^3 and M^v is another of M^1 or M^2 or M^3 , and M^y is the third (co)monomer,

p for each block is independently selected such that the number average molecular weight of the copolymer is up to 1,000,000 g/mol; and,

(co)polymers of this topology comprising four or more comonomers, and:

of the formulas:



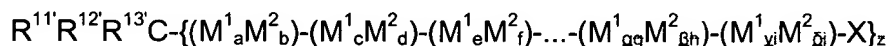


wherein $\{(M^1)_p-X\}$, $\{(M^1)_p-(M^2)_p-X\}$, $\{(M^1)_p-(M^2)_p-(M^3)_p-X\}$, and $\{(M^1)_p-(M^2)_p-(M^3)_p-\dots-(M^t)_p-X\}$ are polymer chains, z is from 3 to 6; $R^{11'}$, $R^{12'}$ and $R^{13'}$ are the same as R^{11} , R^{12} and R^{13} as previously defined with the proviso that $R^{11'}$, $R^{12'}$ and $R^{13'}$ combined contain from together comprise an additional 2 to 5 of the polymer chains enclosed in brackets attached thereto and the C has only one of the polymer chains enclosed in square brackets attached thereto, where X is as defined above;

M^1 , M^2 , M^3 , ... M^t , p , and t are as defined above; and

and copolymers comprising a block or graft with the above composition; and

of the formula:

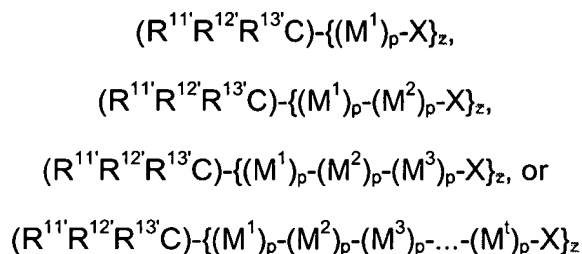


wherein $\{(M^1_aM^2_b)-(M^1_cM^2_d)-(M^1_eM^2_f)-\dots-(M^1_{\alpha g}M^2_{\beta h})-(M^1_{\gamma i}M^2_{\delta j})-X\}$ is a polymer chain, z is from 2 to 6; R^{11} , R^{12} , R^{13} are as defined above, M^1 and M^2 are as defined above and where $R^{11'}$, $R^{12'}$ and $R^{13'}$ are the same as R^{11} , R^{12} and R^{13} with the proviso that $R^{11'}$, $R^{12'}$ and $R^{13'}$ combined have from together comprise an additional 1 to 5 of the polymer chains enclosed in brackets attached thereto and the C has only one of the polymer chains enclosed in square brackets attached thereto, and

a , b , c , d , e , f , ... up to i and j , α , β , γ , δ and such parameters for any intervening blocks are molar percentages of monomer in each block and are non-negative numbers independently selected such that $a + b = c + d = 100\%$, and any or all of $(e + f)$, $(\alpha g + \beta h)$ and $(\gamma i + \delta j) = 100\%$ or 0, wherein the $a:b$ ratio is from 100:0 to 0:100, the $c:d$ ratio is from 95:5 to 5:95, such that $c <$

a and d > b, and where applicable, the e:f ratio is from 90:10 to 10:90, such that e < c and f > d, and the endpoints of the molar ratio ranges of first monomer to second monomer in successive blocks progressively decrease or increase by 5 such that the e:f ratio is from 5:95 to 95:5, such that e ≠ c and f ≠ d, and the $\bar{y}:\bar{d}_j$ ratio is from 0:100 to 100:0, such that $\bar{y}_i \neq e$ and $\bar{d}_j \neq f$.

66. (Amended) The (co)polymer of Claim 64, having a formula:

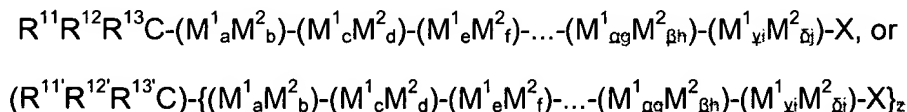


wherein $\{(M^1)_p-X\}$, $\{(M^1)_p-(M^2)_p-X\}$, $\{(M^1)_p-(M^2)_p-(M^3)_p-X\}$, and $\{(M^1)_p-(M^2)_p-(M^3)_p-\dots-(M^t)_p-X\}$ are polymer chains. $R^{11'}$, $R^{12'}$ and $R^{13'}$ are the same as R^{11} , R^{12} and R^{13} as previously defined; with the proviso that $R^{11'}$, $R^{12'}$ and $R^{13'}$ combined contain from together comprise an additional 2 to 5 of the polymer chains enclosed in brackets attached thereto and the C has only one of the polymer chains enclosed in brackets attached thereto, where X is as defined above;

M^1 , M^2 , M^3 , M^t , p and t are as defined above,

z is from 3 to 6, and copolymers comprising a block or graft with the above composition.

67. (Amended) The (co)polymer of Claim 64, having the formulae:



wherein $\{(M^1_aM^2_b)-(M^1_cM^2_d)-(M^1_eM^2_f)-\dots-(M^1_{ag}M^2_{\beta h})-(M^1_{\gamma i}M^2_{\delta j})-X\}$ is a polymer chain. R^{11} , R^{12} , R^{13} ,

and X are as previously defined, and where $R^{11'}$, $R^{12'}$ and $R^{13'}$ are the same as R^{11} , R^{12} and R^{13} with the proviso that $R^{11'}$, $R^{12'}$ and $R^{13'}$ ~~combined have from~~ together comprise an additional 1 to 5 of the polymer chains enclosed in square brackets attached thereto and the C has only one of the polymer chains enclosed in square brackets attached thereto,

M^1 and M^2 are monomer units derived from different radically (co)polymerizable monomers, and a, b, c, d, e, f, ~~... up to i and j~~ α , β , γ , δ and such parameters for any intervening blocks are molar percentages of monomer in each block and are non-negative numbers independently selected such that $a + b = c + d = 100\%$, and any or all of $(e + f)$, $(\alpha\gamma + \beta\delta)$ and $(\gamma\delta + \alpha\beta) = 100\%$ or 0, wherein the a:b ratio is from 100:0 to 0:100, the c:d ratio is from 95:5 to 5:95, such that $c < a$ and $d > b$, and where $e \neq 0$ and $f \neq 0$, the e:f ratio is from 90:10 to 10:90, such that $e < c$ and $f > d$, and the endpoints of the molar ratio ranges of first monomer to second monomer in successive blocks progressively decrease or increase ~~by 5~~ such that the e:f ratio is from 5:95 to 95:5, such that $e \neq c$ and $f \neq d$, and the $\gamma\delta:\alpha\beta$ ratio is from 0:100 to 100:0, such that $\gamma\delta \neq e$ and $\alpha\beta \neq f$, and z is from 2 to 6.